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## Investigation of the factors influencing the wettability of conducting polymers for fluid control in microfluidic devices

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**INVESTIGATION OF THE FACTORS  
INFLUENCING THE WETTABILITY OF  
CONDUCTING POLYMERS FOR  
FLUID CONTROL IN MICROFLUIDIC DEVICES**

A thesis submitted in fulfilment of the  
requirements for the award of the degree

**DOCTOR OF PHILOSOPHY**

from

**UNIVERSITY OF WOLLONGONG**

by

**JENNY HALLDORSSON, BSc (Hons)**

**DEPARTMENT OF CHEMISTRY**

**August, 2007**

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## **CERTIFICATION**

I, Jennifer A. Halldorsson, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry at the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for any qualifications at any other academic institution.

Jenny Halldorsson

August 2007

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## PUBLICATIONS

Causley, J. A., Stitzel, S., Brady, S., Diamond, D. and Wallace, G. G. Electrochemically-induced fluid movement using polypyrrole, *Synthetic Metals*, 151 (2005) 60–64.

## CONFERENCE PRESENTATIONS

Halldorsson, J. A., Spinks, G. M., Brown, H. and Wallace, G. G. Investigation of contact angle, wettability and surface energy of polyterthiophenes for fluid control in microfluidic devices. *Higher Degree Research Students Conference* (oral presentation), University of Wollongong, Wollongong, Australia, 2006.

Causley, J. A., Spinks, G. M. and Wallace, G. G. Investigation of conducting polymers for fluid control in microfluidic systems. *Connect* (oral presentation), Sydney, Australia, 2005.

Causley, J. A., Spinks, G. M., Diamond, D. and Wallace, G. G. Fluid control in microfluidic devices using polypyrrole. *Gordon Research Conference on The Physics and Chemistry of Microfluidics* (poster presentation), Magdlen College, Oxford, United Kingdom, 2005.

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## ABSTRACT

The advent of miniaturised analytical systems has the potential to revolutionise the way in which chemical and biological analyses are made, due to the benefits of reduced reagent consumption, increased sensitivity and decreased analysis times. With increasingly smaller device dimensions comes the need for more efficient methods of controlling fluid flow on the microscale. Electrokinetic techniques, such as electrophoresis and electroosmosis, are well suited for delivering analytes and reagents in microfluidic devices, however high driving voltages and power requirements limit the size to which the device may be miniaturised and thus limit the applicability of these flow control methods for portable, hand-held devices. In order to overcome this limitation, an elegant use of surface tension forces which dominate at the microscale is necessary.

Conducting organic polymers, such as polythiophene and polypyrrole, have found widespread use in recent years due to their attractive mechanical properties and processability, in addition to their ability to be reversibly switched between oxidised (conducting) and reduced (insulating) forms. This redox switching may be accompanied by a change in polymer properties such as wettability and surface energy which may be altered dramatically upon external stimulation, commonly in the form of a small applied electrical potential.

The effect of redox switching upon conducting polymer wettability for fluid control in microfluidic devices is the central theme which was explored in this thesis. In particular, the aims of this thesis were to characterise the wettability of conducting polymers and investigate the factors which influence it, as well as explore the use of



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conducting polymers for fluid control in simple, dynamically controlled microfluidic devices, based on the change in wetting properties upon *in-situ* electrochemical redox switching. The role of polymer oxidation state, film thickness, polymerisation substrate and the configuration of the electrochemical cell used for fluid control were considered. Goniometry and tensiometry were used to characterise polymer wetting properties, while microscopy techniques (scanning electron microscopy, atomic force microscopy and optical profilometry) were used to probe the morphology of polymer and understand the role of roughness on conducting polymer wettability and fluid movement. The electrochemical properties of polymers were characterised by cyclic voltammetry, while Raman spectroscopy was employed to gain insight into the role of water and film thickness in determining the oxidation state of polyterthiophene in Chapter 3.

The insights gained during polymer wettability characterisations were extended to investigate surface tension-induced fluidic control using electrochemical cells in both channel-based and droplet-based configurations upon the application of a small voltage. The knowledge gained during the course of this study should form the basis for developing devices which will contribute to interesting solutions for improving flow control on the microscale.

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## ABBREVIATIONS AND NOTATION

$\theta$	equilibrium contact angle
$\theta_a$	advancing contact angle
$\theta_r$	receding contact angle
$\Delta\theta$	contact angle hysteresis; $\theta_a - \theta_r$
$\gamma_l$	surface tension of a liquid
$\gamma_s$	surface tension of a solid
$\gamma_{sl}$	surface tension of the solid-liquid interface
$\gamma_{sv}$	surface tension of the solid in equilibrium with the saturated vapour pressure of the liquid
$\gamma^-$	surface tension arising from electron donation
$\gamma^+$	surface tension arising from electron accepting
$\gamma^{AB}$	surface tension arising from acid-base interactions
$\gamma^d$	surface tension arising from dispersive interactions
$\gamma^{\text{Debye}}$	surface tension arising from Debye interactions
$\gamma^h$	surface tension arising from hydrogen bonding
$\gamma^{\text{Keesom}}$	surface tension arising from Keesom interactions
$\gamma^{\text{London}}$	surface tension arising from London interactions
$\gamma_{lv}$	surface tension of the liquid-vapour interface
$\gamma^{\text{LW}}$	surface tension arising from Lifshitz-van der Waals interactions
$\gamma^m$	surface tension arising from metallic bonding
$\gamma^p$	surface tension arising from polar interactions
$\gamma^{\text{total}}$	total surface tension
$\kappa$	electrical conductivity

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$\mu$ TAS	micro total analysis systems
$\rho$	wetted perimeter of the sample in Wilhelmy balance tensiometry
ACN	acetonitrile
AFM	atomic force microscopy
ATR-FTIR	attenuated total reflection Fourier transform infrared spectroscopy
CDG	contact drop goniometry
CEW	continuous electrowetting
$\text{CH}_2\text{I}_2$	diiodomethane
DCM	dichloromethane
EDL	electrical double layer
EMI.TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide
EWOD	electrowetting on dielectric
$f$	fraction of a solid in contact with a liquid
$F$	weight contribution from the meniscus in Wilhelmy balance tensiometry
$F_b$	buoyancy force
$F_g$	force due to gravity
$F_w$	wetting force
$G$	free energy
GC	glassy carbon
HREELS	high-resolution electron energy loss spectroscopy
ITO	ITO-coated glass
KCl	potassium chloride
NaDBS	sodium dodecylbenzenesulfoante
$\text{NaNO}_3$	sodium nitrate
NapTS	sodium <i>para</i> -toluenesulfonate

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P3BT	poly-3-butylthiophene
P3HT	poly-3-hexylthiophene
P3MT	poly-3-methylthiophene
P3OT	poly-3-octylthiophene
PAn	polyaniline
PDMS	polydimethylsiloxane
PEDOT	poly-(3,4-ethylenedioxythiophene)
PMMA	polymethylmethacrylate
PNiPAAM	poly( <i>N</i> -isopropylacrylamide)
PPy	polypyrrole
PPy.DBS	polypyrrole doped with dodecylbenzenesulfonate
Pt	platinum sheet
Pt-PMMA	platinised polymethylmethacrylate
Pt-PVDF	platinised PVDF membrane
PTTh.ClO <sub>4</sub>	polyterthiophene doped with perchlorate
PTTh-C <sub>60</sub> .ClO <sub>4</sub>	N-methyl-2-(2-[2':5',2''-terthiophen-3'yl]ethenyl)fullero[3,4] pyrrolidine) doped with perchlorate
PTTh-DDO.ClO <sub>4</sub>	poly-(4,4'-didecyloxy-2,2':5',2''-terthiophene) doped with perchlorate
PVDF	polyvinylidenedifluoride
<i>r</i>	roughness
SAM	self-assembled monolayer
SEM	scanning electron microscopy
SERS	surface enhanced Raman spectroscopy
SSIMS	static secondary ion mass spectrometry
TBA.ClO <sub>4</sub>	tetrabutylammonium perchlorate

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TiO <sub>2</sub>	titanium dioxide
TPG	tilting plate goniometry
TTh	2,2':5',2''-terthiophene
TTh-C <sub>60</sub>	N-methyl-2-(2-[2':5',2''-terthiophen-3'yl]ethenyl)fullero[3,4] pyrrolidine
TTh-DDO	4,4'-didecyloxy-2,2':5',2''-terthiophene
W	measured weight (net force)
WBT	Wilhelmy balance tensiometry
XPS	X-ray photoelectron spectroscopy
ZDOI	zero depth of immersion
ZnO	zinc oxide

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